



AFRL-RX-WP-TP-2009-4034

FREEZE-SPRAY DEPOSITION OF LAYERED ALUMINA/ZIRCONIA COMPOSITES (PREPRINT)

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University of Missouri Rolla

JANUARY 2009

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YY) January 2009		2. REPORT TYPE Journal Article Preprint		3. DATES COVERED (From - To) 01 January 2009 – 31 January 2009	
4. TITLE AND SUBTITLE FREEZE-SPRAY DEPOSITION OF LAYERED ALUMINA/ZIRCONIA COMPOSITES (PREPRINT)				5a. CONTRACT NUMBER FA8650-04-C-5704	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 78011F	
6. AUTHOR(S) Qiang Fu, Oratai Jongprateep, Ashlee Abbott, and Fatih Dogan				5d. PROJECT NUMBER 2865	
				5e. TASK NUMBER 25	
				5f. WORK UNIT NUMBER 25100000	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Missouri at Rolla Department of Materials Science and Engineering 1870 Miner Circle Rolla, MO 65409-0970				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RX-WP-TP-2009-4034	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RXLMP	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RX-WP-TP-2009-4034	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Journal article submitted to <i>Materials Science and Engineering B</i> , November 2008. This work was funded in whole or in part by Department of the Air Force contract FA8650-04-C-5704. The U.S. Government has for itself and others acting on its behalf an unlimited, paid-up, nonexclusive, irrevocable worldwide license to use, modify, reproduce, release, perform, display, or disclose the work by or on behalf of the U.S. Government. Technical paper contains color. PAO Case Number and clearance date: 88ABW-2008-0913, 12 November 2008					
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15. SUBJECT TERMS freeze-spray, automated 3-D gantry system, aqueous slurries					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 26	19a. NAME OF RESPONSIBLE PERSON (Monitor) Todd J. Turner 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Freeze-Spray Deposition of Layered Alumina/Zirconia Composites

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Abstract

A novel freeze-Spray Deposition (FSD) method is described for rapid fabrication of layered composites with controlled layer thickness and uniform microstructure. The graded alumina/zirconia composites are fabricated by freeze-spray deposition of ceramic slurries followed by freeze drying. Aqueous slurries with glycerol addition are sprayed on a cooled substrate using an automated 3-D gantry system. Processing parameters such as viscosity of the ceramic slurries, composition and thickness of deposited layers as well as sintering conditions are investigated to improve the fabrication process. Microstructural analysis of the fabricated composites revealed uniform and crack-free transitional layers indicating a strong interfacial bonding between the layers.

Introduction

Functionally graded materials received significant attention in development of ceramic composites with unique physical properties. Various methods have been utilized for fabrication of layered composites, including tape casting [1, 2], slip casting [3], electrophoresis deposition [4], plasma spraying [5], etc. Due to the mismatch of thermal expansion and sintering rate of dissimilar materials, microstructural defects, such as cracks and delamination, often occur in layered ceramics [6-10]. Such processing flaws are complex in thermomechanical origins. It was shown that by controlling heating and cooling rates or by mixing Al_2O_3 and ZrO_2 within the layers, the formation of cracks and delamination can be reduced or completely eliminated [11]. A slower cooling rate could completely relax the stress caused by thermal expansion coefficient mismatch of the graded structures at temperatures $>1200^\circ\text{C}$ in hybrid $\text{Al}_2\text{O}_3/\text{ZrO}_2$ laminates [12]. Creep behavior and damage mechanism of functionally graded composites and thermal barrier coatings were investigated under thermal cycling [13, 14].

Freeze-casting, a process involving freezing of ceramic slurries in a nonporous mold followed by sublimation of the solvent, has been utilized to fabricate complex-shaped ceramics [15-25]. However, fabrication of thin layers by freeze casting to form graded structures is a challenging task. Freeze spray deposition (FSD), a technique which involves spraying of ceramic slurries onto a cold substrate followed by sublimation of the solvent, is introduced in this work to fabricate layered composites at a rapid processing speed.

The present study is aimed at utilizing of the FSD process for rapid processing of alumina/zirconia graded laminar composites with controlled layer thickness and microstructural development. Processing parameters such as composition, concentration and rheological

properties of ceramic slurries as well as sintering conditions of green bodies were studied to improve the microstructural development of layered composites. The sintered composites were characterized by electron microscopy techniques to reveal the microstructural development of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ graded structures.

Experimental Procedure

(1) Slurry Preparation and Rheology Study

Alumina (A16SG: Alcoa, USA) and 5.3 weight% (3 mol%) yttria-stabilized zirconia (Sigma Aldrich, USA) powders were used for preparation of slurries. The average particle sizes of powders were d_{50} : 0.40 μm for alumina and d_{50} : 0.82 μm for zirconia. Alumina and zirconia aqueous slurries with solids loadings ranging from 30-50 vol% were prepared using 1.2 wt% ammonium polymethacrylate (Darvan C: Vanderbilt, USA) and 3 wt% acrylic emulsion polymer (Duramax: Rohm and Haas, USA). The amount of organic additives in weight percentage was calculated based on the weight of the powders. Glycerol (Fisher Scientific, Pittsburg, PA) with the amount of 20 wt% by weight of water was used as a cryoprotectant to prevent the growth of large ice and freezing defects associated with crystallization of water in slurries. To attain a homogeneous slurry mixture, mechanical milling was performed for 24 hours in polypropylene bottles using alumina grinding media. Rheological characterization of the slurries was conducted to evaluate the stability of slurries. Viscosities of the well-dispersed slurries were measured using a rotating concentric cylinder viscometer (Haake, Model VT500) with shear rates varying from 0–500 s^{-1} .

(2) Freeze spray deposition of alumina/zirconia composites

Slurries were prepared by optimizing their viscosity, and solids loading to obtain optimum spray behavior without clogging of the nozzle during spray process. Alumina and zirconia slurries were processed with 45vol % and 35 vol % solids loading, respectively. Thin and uniform layers of the sprayed slurries were achieved under the air pressure of 40 psi, using a spray nozzle (Iwata, Model HP-BCS). Graded alumina/zirconia composites were fabricated by spraying of slurries onto metallic plates cooled with liquid nitrogen. The thickness of each layer was controlled by repetitive spray deposition of slurries on frozen material. A 3-D gantry system (**Fig. 1**) was employed in controlling the height and movement of the spray nozzle. Upon completion of the FSD process, the frozen green compacts were subjected to a 4 Pa vacuum for sublimation of solvent in a freeze dryer (Virtris, Model Genesis 25). Freeze dried samples were isostatically pressed at a pressure of 250MPa to increase the density and strength of green bodies. Following the binder burnout process at 550°C for 1 hour at a heating rate of 1°C/min, the samples were sintered at 1600°C for 2 hours with a heating and cooling rate of 3°C/min.

(3) Characterization

The sintering behavior of freeze-sprayed alumina and zirconia samples was characterized using a dilatometer (Theta, Model Dilamatic II) by measuring the dimensional shrinkage as a function of temperature at temperatures ranging from 100°C to 1500 °C with a heating rate of 5 °C /min. Coefficient of thermal expansion (CTE) of sintered samples was measured using a dilatometer (Orton, Model 1600). Linear dimensional change of the samples upon heating was used to determine the CTE values of the samples. The mean CTE was calculated using data collected between 250°C and 750°C.

Scanning electron microscope, SEM (Hitachi, Model S-4700), equipped with an electron dispersive x-ray spectroscopy (EDS), was employed for compositional analysis and microstructural characterization of grade composites prepared by polishing with a 0.05 μm finish and thermal etching at 1450°C for 30 min.

Results and Discussion

(1) *Rheology Study*

Spray processes of ceramic slurries require a delicate control of rheological properties of slurries particularly with high solids loadings. Alumina and zirconia aqueous slurries with solids loadings ranging from 30 to 50 vol%, with and without glycerol addition were prepared and characterized by viscosity measurements. All slurries used in this study exhibited shear thinning behavior. For a 30 vol % alumina slurry, an increase of the viscosity (at a shear rate of 100s⁻¹) from 20 to 140 mPa/s was observed while the viscosity for a 50 vol % slurry increased from 11 to 65mPa/s with and without glycerol addition, respectively. A typical viscosity curve for a 45 vol% alumina slurry with 20 wt% glycerol is shown in **Fig. 2**.

Results from viscosity measurement also revealed that glycerol, initially added to prevent the growth of large ice and freezing defects, had a significant effect in reduction of viscosity of alumina slurries at high solids loadings. The relative viscosities (shear rate: 100 s⁻¹) of alumina slurries with and without glycerol addition as a function of solids loading are shown in **Fig. 3**. Viscosity data fit well the theoretical curve according to the modified Krieger-Dougherty equation [26, 27]:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-n} \quad (1)$$

whereas η_r : the relative viscosity defined as the viscosity of the suspension, η , divided by the viscosity of the solvent (water) η_L , ϕ is the volume fraction of the particles, ϕ_m is the volume fraction of particles at which the viscosity becomes practically infinite, and n is a fitting parameter. The maximum alumina solids loading predicted by this model was $\phi_m = 66$ vol%, with $n = 3.0$ for alumina slurry without glycerol and 69 vol% with $n = 3.2$ for the slurry containing 20wt% glycerol.

Reduction of the viscosity in slurries with glycerol addition is attributed to a more effective steric stabilization. It was suggested that glycerol may play a crucial role in: i) enhancement of the dispersant's role in overcoming of van der Waals attraction, ii) acting as a lubricant between particles and decreasing the viscosity of the slurry, and iii) interacting with nonionic dispersants to form a micelle structure, which results in an increase of particle-particle separation [28].

(2) Sintering Behavior and Thermomechanical Properties

The sintering density of freeze-sprayed alumina and zirconia samples are shown in **Fig. 4**. While the onset temperature for sintering of both alumina and zirconia is near 1100 °C densification of zirconia was completed at 1400 °C with a linear shrinkage of 21%, On the other hand, densification of alumina required temperatures greater than 1500 °C. A steeper slope in the sintering curve of zirconia suggested a faster sintering rate as compared to that of alumina. Differential densification of alumina and zirconia layers during the sintering process may lead to differential shrinkage between two materials, which may result in warping of the samples. Since densification of zirconia layer takes place at lower sintering temperatures as compared to that of alumina, excessive differential shrinkage due to constrained sintering may also result in crack formation perpendicular to the layers.

To eliminate differential densification associated with sintering rate and thermal expansion mismatch between alumina and zirconia, four transitional layers were deposited. The transitional layers were prepared by mixing of an alumina slurry with 45 vol% solids loading and a zirconia slurry with 35 vol% solids loading at different ratios. Final compositions of the transitional layers are shown in Table 1. The coefficient of thermal expansion (CTE) of alumina-zirconia composites is shown in **Fig. 5**. CTE values for alumina and zirconia were determined as $8.8 \times 10^{-6}/^{\circ}\text{C}$ and $11.3 \times 10^{-6}/^{\circ}\text{C}$, respectively. It was observed that the CTE increases linearly as the volume fraction of zirconia (ranging from 20 to 80 vol%) in alumina increases. The experimental results suggested that the mismatch of CTE between dissimilar materials could be reduced by the presence of transitional layers, which is attributed to reduction of the stress concentration at the interfaces.

(3) Layered Composites

Based on the rheology studies and microstructural evaluation of the samples, alumina and zirconia slurries with glycerol addition were used for fabrication of laminated composites. Laminar alumina and zirconia samples were processed by freeze-spray deposition of graded layers. A typical microstructure of an alumina-zirconia layered composite is shown in **Fig. 6**. The thickness of each layer was in the range of 200-300 μm , which was obtained after spraying for ten times. Each spray corresponded to the formation of layers with a thickness of 20-30 μm . By controlling the solids loading of slurries, the flow rate and the speed of nozzle movement, the layer thickness of a given composition could be adjusted during the FSD process. An abnormal grain growth (AGG) to certain extent and platelike grains were observed in pure alumina (see **Fig. 7 (a)**). The AGG of alumina may be attributed to the presence of certain

impurities such as CaO [29, 30] and SiO₂ [31-33]. As a result of AGG, intergranular pores were trapped within or between the abnormally grown large grains, which inhibited the further densification of the laminate. On the other hand, AGG of alumina in transitional laminates was not readily evident (see **Fig. 7 (b)-(e)**). The presence of a secondary phase, specifically zirconia, was beneficial with respect to inhibition of AGG. Fine zirconia particles are believed to pin the grain boundaries of alumina which, in turn, inhibits the grain boundary migration [34-36]. The pinning effect, therefore, resulted in suppression of the grain growth of the alumina in the composite. **Fig. 7 (a)** reveals that the average grain size of alumina in the Al₈₀-Zr₂₀ layer is significantly smaller (~1-2µm) as compared to that of pure alumina (~5µm). Similarly, the grain growth of alumina in other transitional layers (see **Fig. 7 (b) to (e)**) was also inhibited. A dense and uniform microstructure without cracks and micro-pores was obtained in the transitional laminates. Alumina- zirconia layered structures and other composites may find applications as materials exposed to high temperature gradients. Such composites with complex geometries can be fabricated at rapid processing rates by utilizing of the FSD technique.

Summary

Freeze-spray deposition method was developed for rapid fabrication of laminated composites with controlled layer thickness and uniform microstructure. Alumina-zirconia layered composites were processed using aqueous slurries with glycerol addition under rapid freezing conditions. A differential shrinkage during sintering of alumina and zirconia was reduced by deposition of transitional layers to obtain a compositional gradient. A dense and uniform microstructural development and crack-free interfaces between the layers show the potential of freeze-spray deposition as a method to fabricate layered composite materials for practical applications

Acknowledgement

This work was supported by the Air Force Research Laboratories under contract FA8650-04-C-5704. We thank Drs. M. Leu, G. Hilmas, R. Landers, and S. Reis for useful discussions.

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Table 1: Composition of mixed alumina and zirconia slurries used for deposition of transitional layers

Slurry	Composition (vol%)
Al80-Zr20	80 Al ₂ O ₃ - 20 ZrO ₂
Al60-Zr40	60 Al ₂ O ₃ – 40 ZrO ₂
Al40-Zr60	40 Al ₂ O ₃ – 60 ZrO ₂
Al20-Zr80	20 Al ₂ O ₃ – 80 ZrO ₂

Figure Captions

Fig. 1 Experimental apparatus showing a system employed for the sample fabrication process

Fig. 2 Rheological behavior of 45vol% Al_2O_3 slurry with glycerol

Fig. 3 Relative viscosity at a shear rate of 100 s^{-1} as a function of volume fraction for alumina slurries with and without glycerol

Fig. 4 Linear shrinkage versus temperature during constant heating rate sintering for Al_2O_3 and ZrO_2

Fig. 5 Coefficient of thermal expansion (CTE) of alumina/zirconia composites as a function of zirconia volume fraction in alumina

Fig. 6 Microstructure of the sintered alumina/zirconia composites

Fig. 7 Microstructure between alumina/zirconia laminates revealing crack-free interfaces

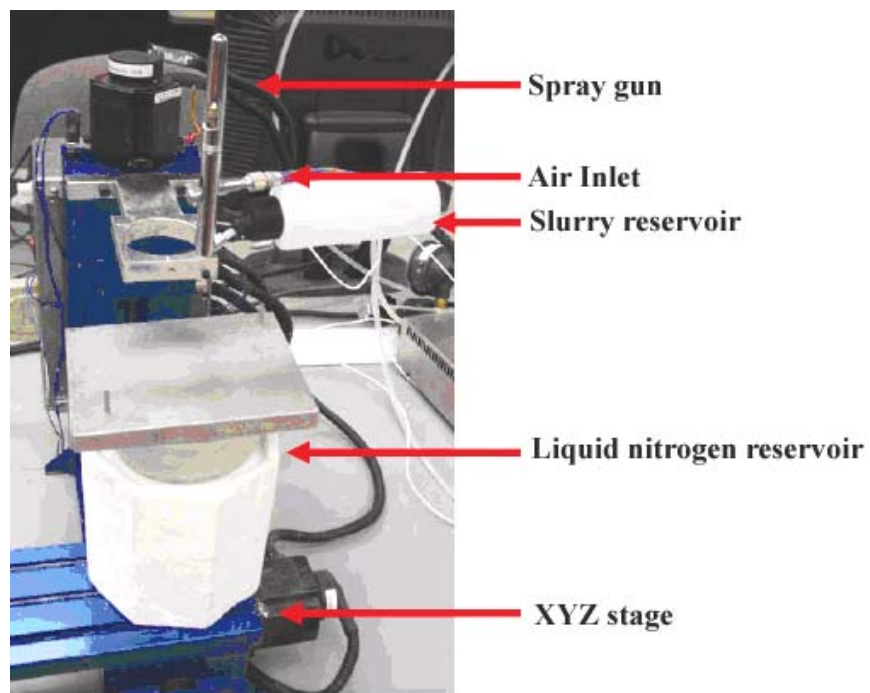


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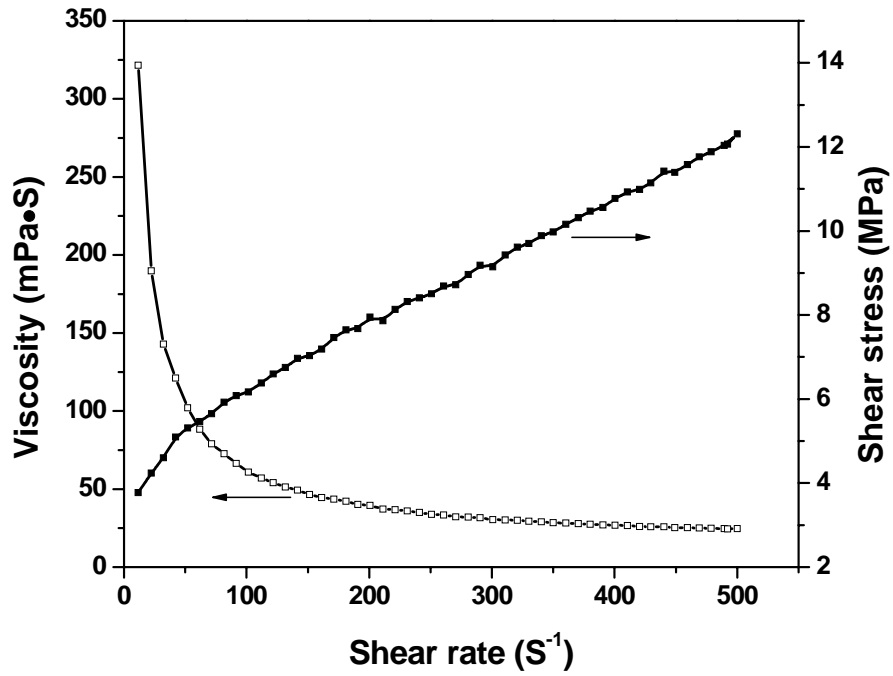


Fig. 2 Rheological behavior of 45vol% Al_2O_3 slurry with glycerol

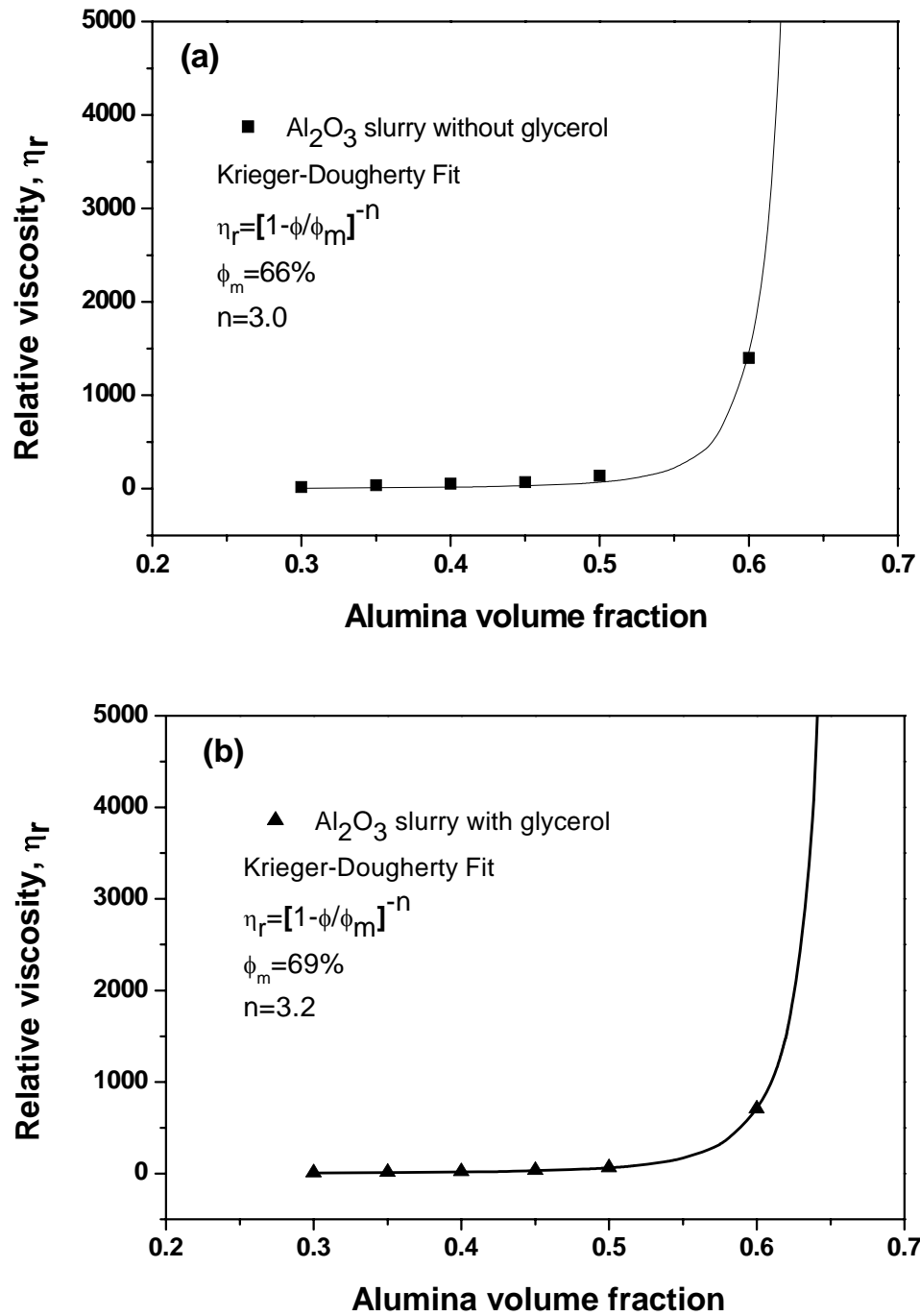


Fig. 3 Relative viscosity at a shear rate of 100 s^{-1} as a function of volume fraction for alumina slurries with and without glycerol

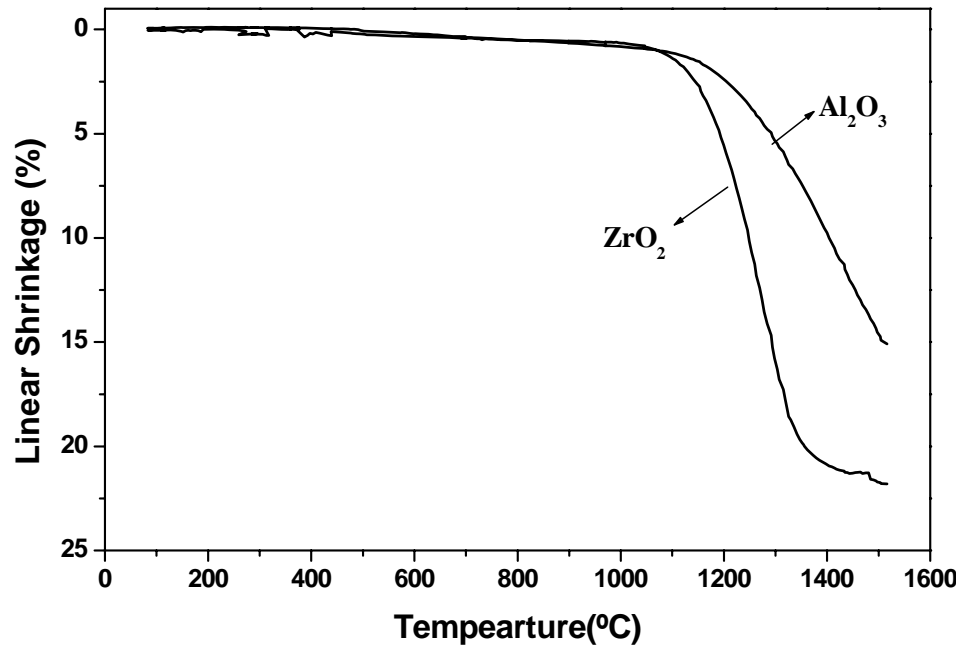


Fig. 4 Linear shrinkage was a functions of temperature during constant heating rate sintering for Al_2O_3 and ZrO_2

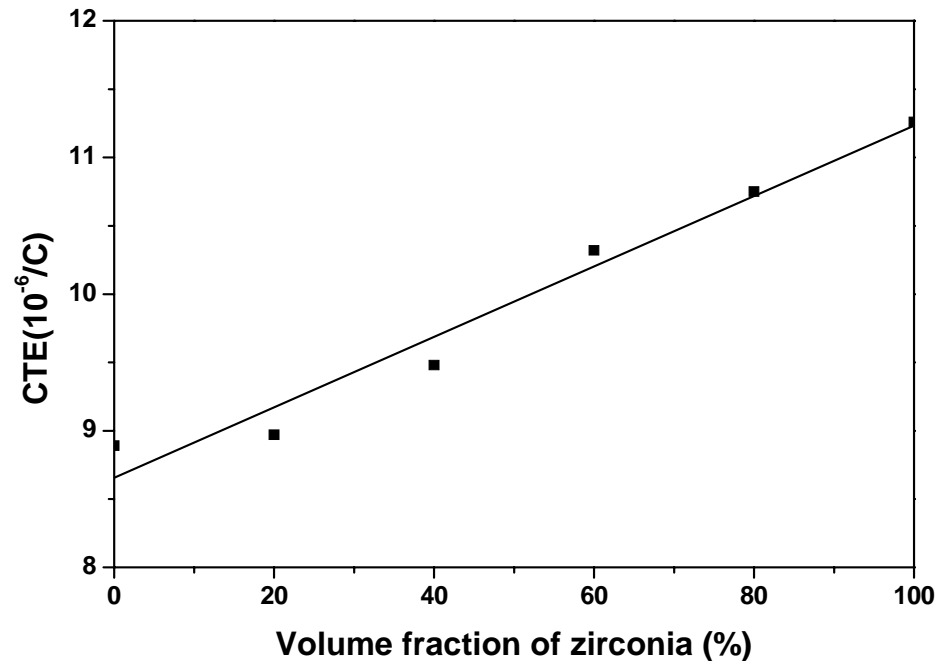


Fig. 5 Coefficient of thermal expansion (CTE) of alumina/zirconia composites as a function of zirconia volume fraction in alumina

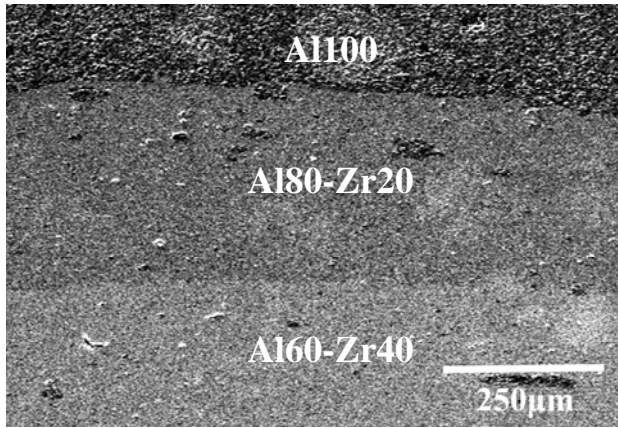


Fig. 6 Microstructure of the sintered alumina/zirconia composites

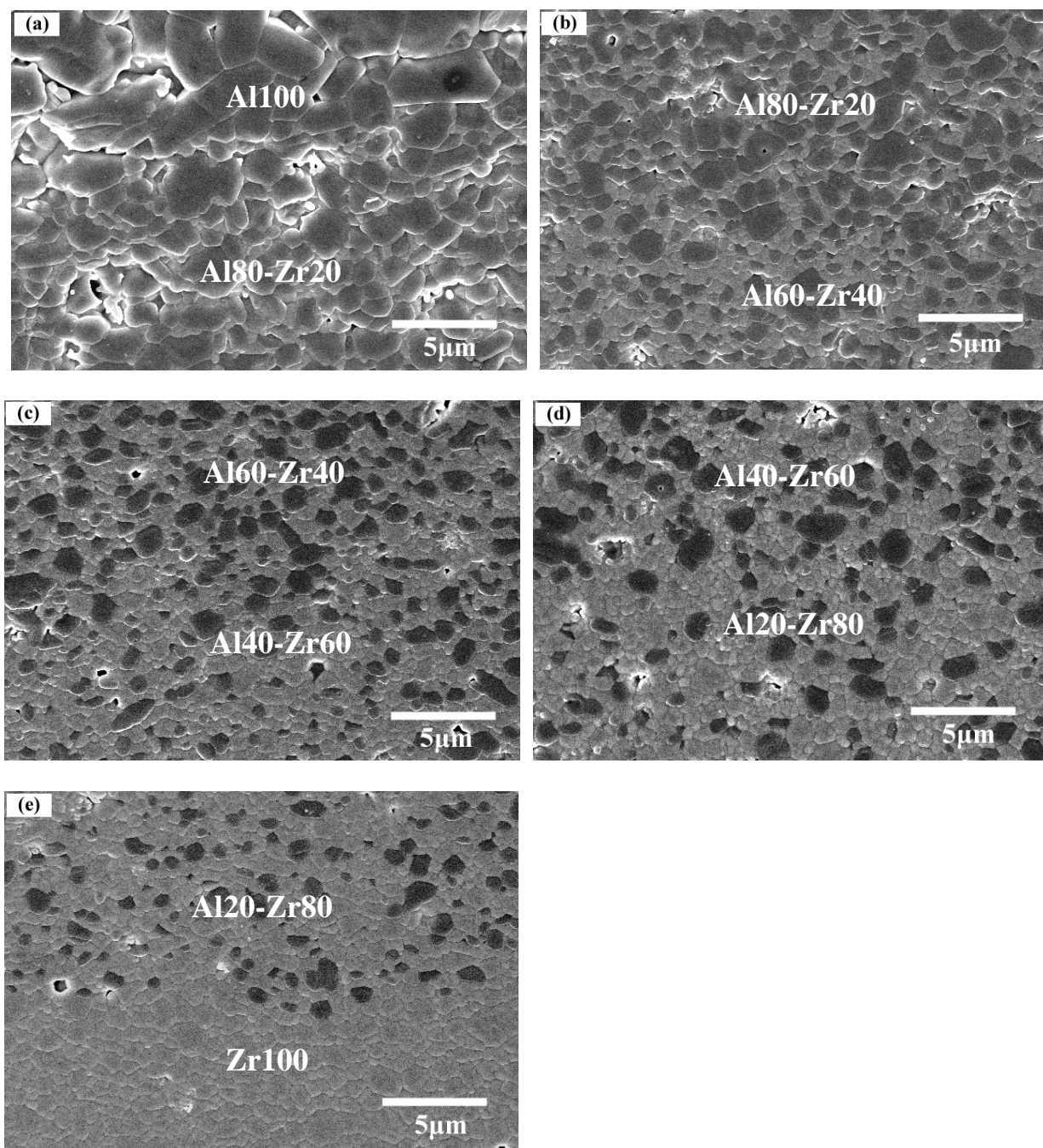


Fig. 7 Microstructure between alumina/zirconia laminates revealing crack-free interfaces